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Anisotropy and anomaly of phonon transport in glycine derivatives

M Gaafar
Department of Physics, Faculty of Science,
Alexandria University, Egypt

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Abstract : Thermal conductivity λ_T of glycine G and its sulphate derivative $G_3H_2SO_4$ along the principal directions, in the temperature range between 300 K and 350 K were measured. The measurements exhibit that the phonon thermal conductivity λ_{ph} is dominant in these compounds. As the crystals are monoclinic, then one thermal conductivity component λ_3 coincides with *b*-axis, while the other two orthogonal components λ_1 and λ_2 fall in (010) plane. Variations of their values exhibit anisotropy of phonon transport within the crystals. Anomaly of the component $\lambda_{ph\text{-}3}$ of $G_3H_2SO_4$ along the ferroelectric axis (*b*-axis) at T_c = 322 K was observed and an explanation of its origin is offered, also other phonon scattering mechanisms in this temperature range is dealt with.

Keywords : Phonon transport, phase transition, glycine and its sulphate derivatives

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The crystal structure of each of glycine (G) compound and its sulphate derivative $G_3H_2SO_4$ has been determined. G-crystal is monoclinic [1] with $a = 5.102$ A, $b = 11.97$ A, $c = 5.475$ A, $\beta = 111°7'$, $z = 4$, $P2_1/n$. The carbon and oxygen atoms are nearly planar. $G_3H_2SO_4$ crystal is also monoclinic [2] with $a = 9.41$ A, $b = 12.64$ A, $c = 5.74$ A, $\beta = 110°23'$, $z = 8$, $P2_1$. This compound is ferroelectric [3] with uniaxial ferroelectric axis (*b*-axis). It belongs to the space group $P2_1$, in its ferroelectric phase below T_c, changing to paraelectric phase with space group $P2_1/m$ above T_c, where the spontaneous polarization disappears. The mirror symmetry is attained by the arrangement of atoms around the mirror planes. The structure is still in monoclinic system below and above T_c [4]. The unit cell of this compound contains two chemical groups with 8 units, six independent glycine molecules (G_I, G_{II}, G_{III}) and two sulphate ions. The deduced 'flipping' [2] of the tightly hydrogen bond between O_{II} and O_{III} with associated rotation of sulphate ions, helps to account for the large spontaneous polarization.

Detailed dielectric [5,6] and thermal studies [7,8] showed that the ferroelectric–paraelectric (order-disorder) transition is of second order and exhibit anomalous behavior at T_c along *b*-axis. Continuous studies in this interesting range of temperature around T_c is important to show the effect of this phase transition on the phonon transport, which is the aim of this article and a part of our work to study the different scattering mechanism of phonon transport in solids [9–12].

Glycine crystals (NH_2CH_2COOH) [denoted by G], were grown by slow evaporation from aqueous solution. They were prismatic and elongated along [001]. The sulphate derivatives of glycine $(NH_2CH_2COOH)_3\ H_2SO_4$ [denoted by $G_3H_2SO_4$] was prepared by mixing the stoichiometric ratio of H_2SO_4 with a hot solution of chemically pure glycine. The salts were precipitated from these solutions by cooling. The crystal has a pronounced cleavage plane parallel to (010) plane. Prior to each series of measurements, it is clearly important to polish carefully the surface on which the indentation be applied. The investigated crystals are of dimensions in order of 4 mm × 4 mm × 1 mm. To improve the reproducibility of the experiment, the sample was subjected previously to a careful thermal treatment. It was annealed at 350 K for 24 hours and then slowly cooled at a rate of 0.5 K/min from 350 K to 324 K. In the region of phase transition (324 to 320 K), the cooling rate was reduced to 0.05 K/min to eliminate thermal shocks in the nucleation process of the ferroelectric domain structure then the rate was raised again to 0.5 K/min till the room temperature.

The thermal conduction λ_T was measured using the steady state method. The apparatus was prepared carefully to minimise heat loss by radiation. Calibrated thermocouple P_t–P_t/13% Rh was used to measure the temperature difference ΔT and the average temperature of the sample. The power loss in the heater and thermocouple wires (of optimum lengths) was accurately corrected. The uncertainty in the magnitude of conductivity data is estimated to be ± 7%. The electrical conductivity σ was measured using the apparatus mentioned in our previous work [13]. The accuracy of the measurements is ± 13%.

The measurements of thermal conductivity λ_T as well as the electrical resistivity ρ of glycine G and its sulphate derivative $G_3H_2SO_4$ along the principal directions at 300 K are reported. The electrical measurements were used to calculate the electronic part of the thermal conductivity λ_e, under the assumption of elastic scattering of electrons, using the relation

$$\lambda_c(T) = L_0\ T/\rho, \tag{1}$$

where T is the absolute temperature and L_0 is the Wiedemann-Franz ratio [2.45×10^{-8} WΩ/K] for electron dominance of thermal transport. This low value of λ_e shows that the contribution of the total λ_T is mainly due to transfer of energy by

lattice vibrations which take place in insulating solids [14]. The total heat conduction $\lambda_T(T)$ is given by

$$\lambda_T(T) = \lambda_{ph}(T) + \lambda_{photon}(T) + \lambda_c(T). \tag{2}$$

This means that the contribution of the thermal conduction process at high temperature may be attributed to the presence of three conduction mechanisms :

1 Phonon heat conduction λ_{ph} which depends on the lattice vibration.

2 Photon heat conduction λ_{photon} which depends strongly on the optical properties of the sample and can be given in the form [15] :

$$\lambda_{photon}(T) = \frac{16}{3}\frac{\sigma n_i^2 T^3}{\alpha_i} \; Wm^{-1}K^{-1}, \tag{3}$$

where σ (5.67×10^{-8} J/K^4 m^2 s) is the Stefan-Boltzmann constant, α_i (α_3 = 369.6 m^{-1}, $\alpha_1 \approx \alpha_2 \approx$ 386.2 m^{-1}) are the absorption coefficients n_i (n_3 = 1.51, $n_1 \approx n_2 \approx$ 1.63) are the refractive indices at 300 K and T is the absolute temperature.

3 Electronic contribution of heat conduction λ_c which has very small value (in order of 10^{-12} m Wm^{-1}K^{-1}) and is completely neglected in the present case.

By using eqs. (1–3), the thermal conductivity of phonons were calculated and given in Table 1.

Table 1. Axial phonon thermal conductivities and anisotropies (mW/mK) of G and G$_3$H$_2$SO$_4$.

Compound	$\lambda_{ph\text{-}1}$	$\lambda_{ph\text{-}2}$	$\lambda_{ph\text{-}3}$	$\Delta\lambda_{(010)}$	$\Delta\lambda_{cryst}$
G	385	382	350	3	32.5
$G_3H_2SO_4$	467	462	435	5	29

These results show that the phonon thermal conductivity $\lambda_{ph\text{-}3}$ along b-axis is less than both $\lambda_{ph\text{-}1}$ or $\lambda_{ph\text{-}2}$ of the two compounds in (010) plane, in which $\lambda_{ph\text{-}1}$ direction is inclined to [001] direction by 48° and 46° for the two compounds respectively. Variations of λ_{ph} values lead to thermal anisotropy within the crystal in the form

$$\Delta\lambda_{cryst.} = \frac{\lambda_{ph\text{-}1} + \lambda_{ph\text{-}2}}{2} - \lambda_{ph\text{-}3}.$$

The value of the thermal anisotropy $\Delta\lambda_{(010)} = \lambda_{ph\text{-}2} - \lambda_{ph\text{-}1}$ in (010) plane is very little and nearly isotropic thermal vibration of atoms is expected. Comparison of λ values of glycine and its sulphate derivative, Table 1 shows that the addition of sulphate ion improves the thermal conductivity of glycine and freezing in ferroelectric properties in the derivative

sulphate compound as shown below. Continuous measurements of thermal conductivity of the two compounds in the temperature range from 300 K to 350 K exhibit no anomaly except for $G_3H_2SO_4$ compound along the b-axis at T_c = 322 K [see Figure 1]. This anomalous behaviour was also detected during the measurement of the other physical properties of this compound [5–8]. Slight difference $\Delta T_c = \pm 1$ K between T_c in the present work and those in literature may be attributed to the crystal quality, imperfections and experimental errors. The anomaly is a small peak around the Curie point (T_c = 322 K) with relatively narrow temperature range ± 4 K. The slow decrease of $\lambda_{ph\text{-}3}$ in b-direction below T_c is attributed to the scattering of phonons at imperfections, vibrational group of atoms or molecules and domain walls. To explain the enhancement (anomaly) of $\lambda_{ph\text{-}3}$ at T_c, freezing-in of a certain type of vibrational modes in the vicinity of T_c is expected. Relation between the order parameter and the soft mode just below T_c [16], states that only low frequency modes are appreciably excited. If ν is the mode frequency, then the distribution of frequencies $g(\nu)$ is proportional to ν^2 at $\nu \rightarrow 0$ (as $T \rightarrow T_c$), being the result of low frequency. Since the acoustical modes are characterized by a zero frequency at zero wave number, while the optical modes have a finite frequency at zero wave number, the acoustical modes will eventually dominate [17]. A plausible argument [18] was presented

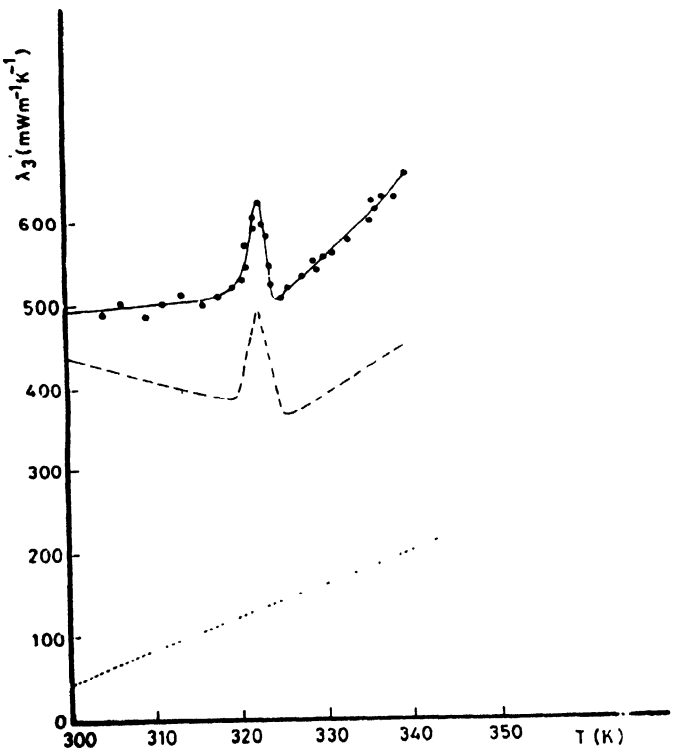

Figure 1. Thermal conductivity λ_3 of $G_3H_2SO_4$ along the b-axis : (- - -) $\lambda_{T\text{-}3}$, (– – –) $\lambda_{ph\text{-}3}$, (· · · ·) $\lambda_{photon\text{-}3}$.

to show that at low frequency, the mean free path of phonon l_{ph} is proportional to ν^{-2} and responds to increase of l_{ph} below T_c to demonstrate the enhancement of $\lambda_{ph\text{-}3}$. In addition, rotation of sulphate ion which is associated with the rapid decrease of the spontaneous polarization across T_c [3], and thus weakly coupled to the lattice, vibrates independently and excess of phonons are excited to enhance $\lambda_{ph\text{-}3}$ just below T_c. Further increase of λ_3 is controlled at $T \approx T_c$ where l_{ph} becomes of the order of magnitude of the translational symmetry distortion, hence decrease of $\lambda_{ph\text{-}3}$ takes place beyond T_c. Again slow increase of $\lambda_{ph\text{-}3}$ above T_c, [see Figure 1] is analogous to λ behaviour in disorder state and then is attributed to disorder scattering [18,11] in which l_{ph} is related with the correlated length among the scattering centres and termed (structure scattering). This mechanism is due to decrease of extended structure defects with raised temperature connected with relaxation of internal stress or decrease of state density [19].

This work exhibits that the thermal conductivity of the two compounds G and $G_3H_2SO_4$ are of dominant phonon character and show anisotropy along their principal axes. Addition of sulphate ion to G compound improves the thermal conductivity of its sulphate derivative and freezing in ferroelectric properties. The derivative compound $G_3H_2SO_4$ shows anomaly of $\lambda_{ph\text{-}3}$ along its ferroelectric b-axis at T_c = 322 K. The anomaly is attributed to dominance of low frequency acoustical mode near T_c. Decrease of $\lambda_{ph\text{-}3}$ below T_c is due to scattering mechanism at imperfection, atoms, molecules or domain walls, above T_c it is termed disorder scattering.

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